Chapter 4

Time-dependent perturbation theory

4.1 The Fermi golden rule

We said that the best way to find out the evolution of quantum states in time is to solve for the eigenstates of the Hamiltonian. However, as we discussed earlier, most Hamiltonians are not amendable to exact diagonalization. In chapter two we have discussed perturbative method to find the eigen-solutions of

$$H = H_0 + V \tag{4.1}$$

when V is weak.

In this chapter we deal with perturbative method to find the time evolution operator of Eq. (4.1) directly. Let us first focus on the case where V is *time independent*. The time evolution operator is given by

$$e^{-i\frac{t}{\hbar}(H_0+V)}. \tag{4.2}$$

To obtain an approximate expression for the time evolution operator when V is weak one might think of an expansion as follow

$$e^{-i\frac{t}{\hbar}(H_0+V)} = \sum_n \frac{1}{n!}\left(-\frac{it}{\hbar}\right)^n (H_0+V)^n. \tag{4.3}$$

In order to obtain $O(V)$ term one might think of expanding $(H_0+V)^n$. However since

$$[H_0, V] \neq 0 \tag{4.4}$$

in general the O(V) expansion of $(H_0 + V)^n$ is not simply nVH_0^{n-1}. Rather we have to keep n terms of different ordering

$$VH_0^{n-1} + H_0VH_0^{n-2} + H_0^2VH_0^{n-3} + ... \tag{4.5}$$

A easier way to obtain an O(V) expansion of the time evolution operator is to break it into many infinitesimal pieces:

$$\begin{aligned} e^{-i\frac{t}{\hbar}(H_0+V)} &= \left[e^{-i\frac{\epsilon}{\hbar}(H_0+V)}\right]^N \\ &= e^{-i\frac{\epsilon}{\hbar}(H_0+V)}...e^{-i\frac{\epsilon}{\hbar}(H_0+V)}e^{-i\frac{\epsilon}{\hbar}(H_0+V)} \end{aligned} \tag{4.6}$$

where

$$N\epsilon = t. \tag{4.7}$$

Now for each $e^{-i\frac{\epsilon}{\hbar}(H_0+V)}$ we can expand to $O(\epsilon)$ as follows[1]

$$e^{-i\frac{\epsilon}{\hbar}(H_0+V)} \approx e^{-i\frac{\epsilon}{\hbar}H_0}\ e^{-i\frac{\epsilon}{\hbar}V} \approx e^{-i\frac{\epsilon}{\hbar}H_0}\Big(1 - i\frac{\epsilon}{\hbar}V\Big). \tag{4.10}$$

Substitute the above result into Eq. (4.6) we obtain

$$e^{-i\frac{t}{\hbar}(H_0+V)} = e^{-i\frac{t}{\hbar}H_0} - \frac{i\epsilon}{\hbar}\sum_{j=1}^{N}\left[e^{-i\frac{\epsilon}{\hbar}H_0}\right]^{N-j} V \left[e^{-i\frac{\epsilon}{\hbar}H_0}\right]^{j}. \tag{4.11}$$

As $\epsilon \to 0$ the above expression approaches

$$e^{-i\frac{t}{\hbar}(H_0+V)} = e^{-i\frac{t}{\hbar}H_0} - \frac{i}{\hbar}\int_0^t d\tau e^{-\frac{i}{\hbar}(t-\tau)H_0}\ V\ e^{-\frac{i}{\hbar}\tau H_0}. \tag{4.12}$$

---

[1] In general

$$e^A e^B \neq e^{A+B}. \tag{4.8}$$

The equality holds only when $[A, B] = 0$. However even when $[A, B] \neq 0$

$$e^{\epsilon A}e^{\epsilon B} = e^{\epsilon(A+B)} \tag{4.9}$$

to $O(\epsilon)$ because $[\epsilon A, \epsilon B] = O(\epsilon^2)$.

Eq. (4.12) form the basis of the first order time dependent perturbation theory.

Suppose at time 0 the system is in the eigenstate $|i\rangle$ of H_0 ($H_0|i\rangle = \epsilon_i|i\rangle$). Question: at time t what is the probability that the system made a transition to eigenstate $|f\rangle$ of H_0? The probability amplitude of this transition is given by

$$\begin{aligned} A_{fi} &= \langle f|e^{-i\frac{t}{\hbar}H_0}|i\rangle - \frac{i}{\hbar}\int_0^t d\tau \langle f|e^{-\frac{i}{\hbar}(t-\tau)H_0}\ V\ e^{-\frac{i}{\hbar}\tau H_0}|i\rangle \\ &= e^{-i\epsilon_i t/\hbar}\delta_{fi} - \frac{i}{\hbar}\int_0^t d\tau e^{-\frac{i}{\hbar}(t-\tau)\epsilon_f}\langle f|V|i\rangle e^{-\frac{i}{\hbar}\tau\epsilon_i}. \end{aligned} \tag{4.13}$$

For the case of different initial and final states we have

$$A_{fi}(t) = -\frac{i}{\hbar}\int_0^t d\tau e^{-\frac{i}{\hbar}(t-\tau)\epsilon_f}\langle f|V|i\rangle e^{-\frac{i}{\hbar}\tau\epsilon_i}. \tag{4.14}$$

The transition probability is

$$\begin{aligned} P_{fi}(t) &= |A_{fi}(t)|^2 = \frac{1}{\hbar^2}\Big|\int_0^t d\tau e^{\frac{i}{\hbar}\tau\epsilon_f}\langle f|V|i\rangle e^{-\frac{i}{\hbar}\tau\epsilon_i}\Big|^2 \\ &= \frac{1}{\hbar^2}\Big|\int_0^t d\tau e^{\frac{i}{\hbar}\tau(\epsilon_f-\epsilon_i)}\langle f|V|i\rangle\Big|^2. \end{aligned} \tag{4.15}$$

Using Eq. (4.15) we can rewrite $P_{fi}(T)$ as

$$P_{fi}(T) = \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2\int_0^T d\tau\int_0^T d\tau' e^{\frac{i}{\hbar}(\tau-\tau')(\epsilon_f-\epsilon_i)}. \tag{4.16}$$

We can change the integration variable to

$$\tau_+ = \tau + \tau' \quad \tau_- = \tau - \tau' \tag{4.17}$$

and rewrite Eq. (4.18) as

$$P_{fi}(T) = \frac{1}{2\hbar^2}|\langle f|V|i\rangle|^2\int_0^{2T} d\tau_+\int_{-T}^{T} d\tau_- e^{\frac{i}{\hbar}\tau_-(\epsilon_f-\epsilon_i)}. \tag{4.18}$$

Since the integrand in Eq. (4.18) does not depend on τ_+ we have

$$P_{fi}(T) = \frac{T}{\hbar^2}|\langle f|V|i\rangle|^2\int_{-T}^{T} d\tau_- e^{\frac{i}{\hbar}\tau_-(\epsilon_f-\epsilon_i)}, \tag{4.19}$$

Thus the transition probability grows linearly with the waiting time t. The transition rate is given as

$$W_{fi} = \frac{P_{fi}(T)}{T}. \tag{4.20}$$

Using the above result we obtain

$$W_{fi} = \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2 \int_{-T}^{T} d\tau_- e^{\frac{i}{\hbar}\tau_-(\epsilon_f - \epsilon_i)}. \tag{4.21}$$

One convenient way of performing the integral in Eq. (4.21) is to introduce a cutoff factor $e^{-\gamma|t|}$ ($\gamma = 1/T$) into the time integral of Eq. (4.21) and rewrite Eq. (4.21) as follow

$$\begin{aligned} W_{fi} &= \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2 \int_{-\infty}^{\infty} d\tau_- e^{-\gamma|t|} e^{\frac{i}{\hbar}\tau_-(\epsilon_f - \epsilon_i)} \\ &= \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2 \frac{2\gamma}{\gamma^2 + (\epsilon_f - \epsilon_i)^2/\hbar^2} \\ &= \frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2 \frac{1}{\pi}\frac{\Gamma}{(\epsilon_f - \epsilon_i)^2 + \Gamma^2}, \end{aligned} \tag{4.22}$$

where

$$\Gamma = \hbar\gamma. \tag{4.23}$$

The function

$$\Delta_\Gamma(\epsilon_f - \epsilon_i) = \frac{1}{\pi}\frac{\Gamma}{(\epsilon_f - \epsilon_i)^2 + \Gamma^2} \tag{4.24}$$

is call the Lorentzian. It has the property that

$$\int_{-\infty}^{\infty} \Delta_\Gamma(\epsilon) d\epsilon = 1 \tag{4.25}$$

and that

$$\lim_{\Gamma \to 0} \Delta_\Gamma(\epsilon_f - \epsilon_i) \to \delta(\epsilon_f - \epsilon_i). \tag{4.26}$$

Thus we have

$$W_{fi} = \frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2 \Delta_\Gamma(\epsilon_f - \epsilon_i). \tag{4.27}$$

Eq. (4.27) is the famous Fermi golden rule. Two things needs to be said about Eq. (4.27).

The meaning of Γ

It is important to clarify the meaning of Γ in Eq. (4.27). We recall that Γ is proportional to γ which is the inverse of the time we use to compute the average transition probability, or the transition rate. An immediate question is what value of γ should we use?

Let us answer this question by considering an explicit example - the decay of an excited state of a atom. Imagine that you have solved the atomic eigenvalue problem and have obtained all the exact eigen energies and eigen wavefunctions of an atom. Suppose the atom is absolutely isolated from everything else in the universe, then if it is in an excited state at time zero, it will stay there forever. However, an absolutely isolated atom does not exist ! As you have learned, light originates from "electromagnetic oscillation", or as commonly put, electromagnetic wave. Photons are the quanta of the electromagnetic oscillation. In an absolute dark space, the electromagnetic oscillators are in their ground state. However in quantum mechanics an oscillator will have zero-point oscillation even in the ground state. It turns out that this zero point oscillation is sufficient to cause an atom to decay. Such a decay rate can be computed using Eq. (4.27) where the perturbation, V, is the interaction between the atom and the electromagnetic oscillators. However, in reality the atom interacts with more things than just the electromagnetic field. For example, suppose the atom in question is one out of many atoms in a atomic gas. Atomic collisions can also cause the atom to decay from its excited state. If our purpose is to understand the decay rate caused by the interaction between an atom and the electromagnetic field, the collision-induced decay is not what we are interested in. How do we remove such complication from our consideration? Suppose the collision causes a finite life time T for the atomic excited state. Such a life time becomes longer as the density of the gas becomes smaller.[2] Imagine that we compute the electromagnetic-induced transition probability. Suppose the atom is in

[2]Because the probability of atomic collision goes down as the density goes down.

the excited state at time zero. As time elapses, both the interaction with the electromagnetic field and atomic collision can induce decay. However at time much smaller than the life time T discussed above, the effect of atomic collision can be ignored. In other words for $t < T$ we can ignore the presence of atomic collision to a good approximation. In this case the γ we should use in Eq. (4.23) is $1/T$!

The above example illustrate where Γ comes from. In general the Hamiltonian we use to describe a quantum system is only an approximate. This is because inevitably such a system interact with the environment. Such interaction causes a finite life time for the eigenstates. The Γ we should use in Eq. (4.27) is the inverse of such life time.

After understanding the meaning of Γ in Eq. (4.27) you probably also realized that it is a quantity that is difficult to estimate.[3]

"Approximate energy conservation"

The function $\Delta_\Gamma(\epsilon_f - \epsilon_i)$ in Eq. (4.27) has the effect of suppressing the transition rate unless

$$|\epsilon_f - \epsilon_i| < \Gamma. \tag{4.28}$$

Thus for very small Γ it imposes the condition of approximate energy conservation. You might ask how can it imposes only an approximate energy conservation? is'nt energy *exactly* conserved? Indeed, energy is exactly conserved, as long as you include the environment in the consideration. In Eq. (4.27) the energy does not include that of the environment. The fact that energy is only approximately conserved simply reflects the fact that there can be *energy exchange* between the system of interest and the environment.

When to use the delta-function version of Eq. (4.27)?

In the text books we often regard $\Delta_\Gamma(\epsilon_f - \epsilon_i)$ as a delta function. This replacement assumes that the life time causes by the environment is infinite. In that limit, transition can only occurs when the initial

[3]In order to estimate Γ we need to have detailed information of how a given system interact with the environment.

and final state energy are *exactly* the same. You might wonder how can this happen since in most microscopic quantum system the energy levels are discrete. In that case does'nt Eq. (4.27) give a non-sensible answer, namely the transition rate is either zero or infinity?[4]

Indeed, in the limit of $\Gamma \to 0$ sensible application of Eq. (4.27) is restricted to the cases where the final state spectrum is *continuous*, or more precisely, the spacing between energy levels is smaller than Γ. For example, the spectrum of free particle in a box becomes continuous when the size of the box approaches infinity. So when we use the delta function version of Eq. (4.27) we always have in mind the following sequence of limits:

$$\text{Box size } \to 0 \text{ first }, \Gamma \to 0 \text{ second.} \tag{4.29}$$

Now we are ready to discuss some examples where we apply Eq. (4.27).

4.2 Simple scattering theory

In this section we apply Eq. (4.27) to study the scattering of free particle plane waves by a localized potential. The Hamiltonian we shall study is of the following generic form

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}). \tag{4.30}$$

Here the potential is localized in the sense that it is non-zero in a finite spatial region. The question we are interested in is what is the probability per unit time, i.e., transition rate that a incident plane wave with wavevector $\mathbf{k}_i$ will be scattered in to wavevectors fall within an solid angle $d\Omega$ around $\mathbf{k}_f$ (see Fig. (4.1)). According to Eq. (4.27) the transition rate dW is given by[5]

$$dW = \frac{2\pi}{\hbar}\int_{\mathbf{k}-\mathbf{k}_f \in d\Omega} \frac{d^3k}{(2\pi/L)^3}|\langle \mathbf{k}|V|\mathbf{k}_i\rangle|^2 \delta(\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}_i)). \tag{4.31}$$

[4]Infinity occurs when there is degeneracy where $\epsilon_f = \epsilon_i$.

[5]The notation dW reminds us the fact that the transition rate is proportional to $d\Omega$.

In the above, L is the linear dimension of a box within which the entire system is contained. The $\int d^3k/(2\pi/L)^3$ simply reflect that under the boundary condition imposed by the box wall there $\mathbf{k}$ vectors are quantized as

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_3). \tag{4.32}$$

In Eq. (4.31) the matrix element $\langle \mathbf{k}|V|\mathbf{k}_i\rangle$ is given by

$$\langle \mathbf{k}|V|\mathbf{k}_i\rangle = \frac{1}{L^3}\int d^3r e^{i(\mathbf{k}_i-\mathbf{k})\cdot\mathbf{r}}V(\mathbf{r}) = \frac{1}{L^3}V(\mathbf{k}-\mathbf{k}_i). \tag{4.33}$$

Here the $1/L^3$ prefactor originates from the normalization of the plane wave, and $V(\mathbf{k})$ is the Fourier transform of $V(\mathbf{r})$. In the case that $V(\mathbf{r})$ is spherically symmetric, we expect $V(\mathbf{k}-\mathbf{k}_i)$ to depends only on the modulus of $\mathbf{k}-\mathbf{k}_i$, i.e.,

$$V(\mathbf{k}-\mathbf{k}_i) = V(|\mathbf{k}-\mathbf{k}_i|). \tag{4.34}$$

The quantity $|\mathbf{k}-\mathbf{k}_i|$ is given by

$$|\mathbf{k}-\mathbf{k}_i| = (k^2 + k_i^2 - 2kk_i\cos\theta)^{1/2}. \tag{4.35}$$

Here θ is the angle between $\mathbf{k}$ and $\mathbf{k}_i$. On the other hand, the energy delta function in Eq. (4.31) is given by

$$\delta(\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}_i)) = \delta\Big(\frac{\hbar^2k^2}{2m} - \frac{\hbar^2k_i^2}{2m}\Big) = \frac{m}{\hbar^2k_i}\delta(k-k_i). \tag{4.36}$$

Put these together with Eq. (4.31) we have

$$\begin{aligned} dW &= \frac{1}{(2\pi)^2L^3}\frac{m}{\hbar^3k_i}\int_{d\Omega}\sin\theta d\theta d\phi\int k^2dk\Big|V(\sqrt{k^2+k_i^2-2kk_i\cos\theta})\Big|^2\delta(k-k_i) \\ &= \frac{1}{(2\pi)^2L^3}\frac{mk_i}{\hbar^3}d\Omega\Big|V\Big(\sqrt{2k_i^2(1-\cos\theta)}\Big)\Big|^2. \end{aligned} \tag{4.37}$$

The differential cross-section

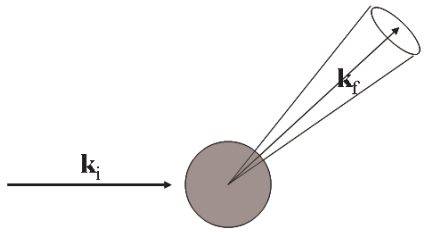

Figure 4.1:

Imagine shooting classical marbles against a hard sphere scatterer. We expect that each particle to be scattered to a different angle, depending on their detailed impact information. In general if the crossectional area of the scatterer intercepting the incoming "marble beam" is σ then the number of particle that will be scattered per unit time is given by

$$\sigma \times \text{incoming particle flux.} \tag{4.38}$$

This is the total scattered particle number in an unit time interval, it includes particles scattered into all possible directions. If we ask per unit time how many particle is scattered into a solid angle $d\Omega$ around a particular direction we will get an answer which is proportional to $d\Omega$ and constitutes a small fraction of Eq. (4.38). In the literature we often define the differential cross-section as

$$d\sigma = \frac{\text{\# of particles scattered into } d\Omega \text{ around a given direction}}{\text{incoming particle flux}} \tag{4.39}$$

since the numerator of Eq. (4.40) is proportional to $d\Omega$ we define

$$\frac{d\sigma}{d\Omega} = \frac{\text{\# of particles scattered into } d\Omega \text{ around a given direction}}{\text{incoming particle flux} \times d\Omega} \tag{4.40}$$

The above classical consideration motivates us to compute the differential cross-section from Eq. (4.37). Since the incoming particle is in a plane wave state, its associated flux is given by

$$f = \frac{1}{L^3} v_i = \frac{1}{L^3} \frac{\hbar k_i}{m}. \tag{4.41}$$

Divide Eq. (4.37) by the above result we obtain

$$\begin{aligned} d\sigma &= \frac{mL^3}{\hbar k_i} \frac{1}{(2\pi)^2 L^3} \frac{mk_i}{\hbar^3} d\Omega \Big| V\Big(\sqrt{2k_i^2(1-\cos\theta)}\Big)\Big|^2 \\ &= \Big(\frac{m}{2\pi\hbar^2}\Big)^2 d\Omega \Big| V\Big(\sqrt{2k_i^2(1-\cos\theta)}\Big)\Big|^2, \end{aligned} \tag{4.42}$$

or equivalently

$$\frac{d\sigma}{d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 \Big| V\Big(\sqrt{2k_i^2(1-\cos\theta)}\Big)\Big|^2. \tag{4.43}$$

Since energy conservation requires

$$|\mathbf{k}_f| = |\mathbf{k}_i| \tag{4.44}$$

it can be shown easily that

$$\sqrt{2k_i^2(1-\cos\theta)} = |\mathbf{k}_f - \mathbf{k}_i| = |\mathbf{q}| \tag{4.45}$$

where $\mathbf{q}$, the wavevector transfer is defined as

$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i. \tag{4.46}$$

In terms of the wavevector transfer Eq. (4.43) reduces to

$$\frac{d\sigma}{d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 |V(\mathbf{q})|^2. \tag{4.47}$$

Eq. (4.47) clearly tells us that by measuring the differential cross-section we are learning information about the Fourier transform of the scattering potential. Thus scattering experiment is an important means to study the properties of the scatterer.

It is useful to analyze the dimension of the differential cross-section. First the Fourier transform of the potential has dimension energy $\times L^3$ Thus the unit of $\frac{d\sigma}{d\Omega}$ is

$$\Big[\frac{d\sigma}{d\Omega}\Big] = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 \times \text{energy}^2 \times \text{length}^6. \tag{4.48}$$

Since

$$\Big[\frac{m}{2\pi\hbar^2} \times \text{length}^2\Big] = \frac{1}{\text{energy}} \tag{4.49}$$

we have

$$\Big[\frac{d\sigma}{d\Omega}\Big] = \text{length}^2. \tag{4.50}$$

Example: scattering by the Yukawa potential

The Yukawa potential is of the form

$$V(r) = g^2\frac{e^{-\kappa r}}{r}. \tag{4.51}$$

It is obvious that Yukawa potential is a central potential, i.e., spherically symmetric. At short distances ($r << \kappa^{-1}$) it is the same as the Coulomb potential. At long distances it falls off to zero exponentially rather than algebraically. This potential could arise from, e.g., the screened Coulomb potential of a foreign charge in a metal. It is straightforward to show that

$$V(\mathbf{q}) = \frac{4\pi g^2}{q^2+\kappa^2}. \tag{4.52}$$

As a result, the differential cross-section caused by the Yukawa potential is given by

$$\frac{d\sigma}{d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2\Big(\frac{4\pi g^2}{q^2+\kappa^2}\Big)^2. \tag{4.53}$$

Eq. (4.53) has two interesting limits.

For $q << \kappa$ Eq. (4.53) approaches

$$\frac{d\sigma}{d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 \Big(\frac{4\pi g^2}{\kappa^2}\Big)^2. \tag{4.54}$$

You will be asked to show in the homework that this has the same form as the differential cross section due to a delta function potential.

In the opposite limit $q >> \kappa$ we have

$$\frac{d\sigma}{d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 \Big(\frac{4\pi g^2}{q^2}\Big)^2, \tag{4.55}$$

which is the differential cross-section due to Coulomb potential.

4.3 Elastic scattering by a target with internal degrees of freedom

In this section we work out the case where the target has internal degrees of freedom. In particular let us consider a target which is made up of N particles. Let $\mathbf{r}_i, ...\mathbf{r}_N$ be the coordinate of this particles and let H_{target} be the Hamiltonian describing the dynamics of them. The total Hamiltonian is given by

$$H = -\frac{\hbar^2}{2m}\nabla^2 + H_{target} + \sum_{j=1}^{N} U(\mathbf{r} - \mathbf{r}_j). \tag{4.56}$$

Here $\mathbf{r}$ is the coordinate of the projectile and we have assumed that the interaction between the projectile and the target particles are identical for $j = 1, ..., N$. In the absence of the last term, the eigenfunction of Eq. (4.56) is the product of plane waves for the projectile and the eigenfunction of the target particles:

$$\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{L^3}} \times \Phi_\alpha(\mathbf{r}_1, ..., \mathbf{r}_N). \tag{4.57}$$

Here α labels the eigenfunctions of the target particles. Elastic scattering is a process in which the projectile is scattered from $\mathbf{k}_i$ to around $\mathbf{k}_f$ while the target particles remain in their ground state

$$\Phi_0(\mathbf{r}_1, ..., \mathbf{r}_N) \tag{4.58}$$

before and after the scattering. In this case we can use Eq. (4.31) with

$$\langle \mathbf{k}|V|\mathbf{k}_i\rangle \rightarrow \langle \mathbf{k}|\langle \Phi_0| \sum_{j=1}^{N} U(\mathbf{r} - \mathbf{r}_j)|\Phi_0\rangle|\mathbf{k}_i\rangle, \tag{4.59}$$

and

$$\delta(\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}_i)) \rightarrow \delta(E_0 + \epsilon(\mathbf{k}) - E_0 - \epsilon(\mathbf{k}_i)), \tag{4.60}$$

where E_0 is the ground state energy of the target particles. The right hand side of Eq. (4.59) is equal to

$$\langle \mathbf{k}|V_{eff}(\mathbf{r})|\mathbf{k}_i\rangle, \tag{4.61}$$

where

$$V_{eff}(\mathbf{r}) = \int d^3r_1...d^3r_N \Phi_0^*(\mathbf{r}_1, ..., \mathbf{r}_N) \sum_{j=1}^{N} U(\mathbf{r} - \mathbf{r}_j)\Phi_0(\mathbf{r}_1, ..., \mathbf{r}_N). \tag{4.62}$$

Repeating the deprivation of the last section we obtain

$$\frac{d\sigma}{d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 |V_{eff}(\mathbf{q})|^2. \tag{4.63}$$

The $V_{eff}(\mathbf{q})$ into Eq. (4.63) is given by

$$\begin{aligned} V_{eff}(\mathbf{q}) \quad &= \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \sum_j \langle \Phi_0|U(\mathbf{r} - \mathbf{r}_j)|\Phi_0\rangle \\ &= U(\mathbf{q}) \sum_j \langle \Phi_0|e^{i\mathbf{q}\cdot\mathbf{r}_j}|\Phi_0\rangle \\ &= U(\mathbf{q}) \sum_j \int d^3r_1...d^3r_N \; e^{i\mathbf{q}\cdot\mathbf{r}_j}|\Phi_0(\mathbf{r}_1, ..., \mathbf{r}_N)|^2 \\ &= U(\mathbf{q})S(\mathbf{q}). \end{aligned} \tag{4.64}$$

Here

$$S(\mathbf{q}) = \sum_j \int d^3r_1 ... d^3r_N \; e^{i\mathbf{q}\cdot\mathbf{r}_j} |\Phi_0(\mathbf{r}_1, ..., \mathbf{r}_N)|^2 \tag{4.65}$$

is called the structure factor of the target. To understand the physical meaning of $S(\mathbf{q})$ we note that

$$\rho(\mathbf{r}) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j) \tag{4.66}$$

is the total density operator of target particles. The ground state expectation value of $\rho(\mathbf{r})$ is given by

$$\bar{\rho}(\mathbf{r}) = \langle\Phi_0|\rho(\mathbf{r})|\Phi_0\rangle = \int d^3r_1 ... d^3r_N \; \sum_j \delta(\mathbf{r} - \mathbf{r}_j) |\Phi_0(\mathbf{r}_1, ..., \mathbf{r}_N)|^2. \tag{4.67}$$

The structure factor is the Fourier transform of $\bar{\rho}(\mathbf{r})$, namely,

$$S(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \bar{\rho}(\mathbf{r}). \tag{4.68}$$

Using Eq. (4.67) it is simple to prove that $S(\mathbf{q})$ is given by Eq. (4.65). Thus for *elastic* scattering by target with internal degrees of freedom we have

$$\frac{d\sigma}{d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 \; |U(\mathbf{q})|^2 \; |S(\mathbf{q})|^2. \tag{4.69}$$

Thus the elastic scattering cross section contains information about the interaction potential between the projectile and the target particles, $U(\mathbf{r})$, as well as the ground state distribution of the target particles.

4.4 Inelastic scattering by a target with internal degrees of freedom

In the previous section we assumed that the before and after the scattering the target particles remain in their ground state. In this section we allow the target to be excited after the scattering process. Thus

$$\frac{e^{i\mathbf{k}_i\cdot\mathbf{r}}}{\sqrt{L^3}} \times \Phi_0(\mathbf{r}_1, ..., \mathbf{r}_n) \tag{4.70}$$

is the initial state and

$$\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{L^3}} \times \Phi_\alpha(\mathbf{r}_1, ..., \mathbf{r}_n) \tag{4.71}$$

is the final state.[6] In this case we can use Eq. (4.31) with

$$\langle \mathbf{k}|V|\mathbf{k}_i\rangle \to \langle \mathbf{k}|\langle\Phi_\alpha|\sum_{j=1}^{N} U(\mathbf{r}-\mathbf{r}_j)|\Phi_0\rangle|\mathbf{k}_i\rangle, \tag{4.72}$$

and

$$\delta(\epsilon(\mathbf{k})-\epsilon(\mathbf{k}_i)) \to \delta(E_\alpha+\epsilon(\mathbf{k})-E_0-\epsilon(\mathbf{k}_i)) = \delta(\Delta_\alpha+\epsilon(\mathbf{k})-\epsilon(\mathbf{k}_i)), \tag{4.73}$$

where $\Delta_\alpha = E_\alpha - E_0$ is the excitation energy of the αth target state. The right hand side of Eq. (4.72) is equal to

$$\langle \mathbf{k}|V_{eff}(\mathbf{r})|\mathbf{k}_i\rangle, \tag{4.74}$$

where

$$V_{eff}(\mathbf{r}) = \int d^3r_1...d^3r_N \Phi^*_\alpha(\mathbf{r}_1, ..., \mathbf{r}_N)\sum_{j=1}^{N} U(\mathbf{r}-\mathbf{r}_j)\Phi_0(\mathbf{r}_1, ..., \mathbf{r}_N). \tag{4.75}$$

The scattering rate where the momentum of the exiting projectile is within $d\Omega$ of $\mathbf{k}_f$ is

$$\begin{aligned} dW &= \frac{2\pi}{\hbar}\int_{\hat{k}-\hat{n}\in d\Omega}\frac{d^3k}{(2\pi/L)^3}|\langle \mathbf{k}|V_{eff}|\mathbf{k}_i\rangle|^2\delta(\epsilon(\mathbf{k})+\Delta_\alpha-\epsilon(\mathbf{k}_i)) \\ &= \frac{2\pi}{\hbar}\frac{L^3}{(2\pi)^3}d\Omega\int k^2dk|\langle \mathbf{k}|V_{eff}|\mathbf{k}_i\rangle|^2\frac{m}{\hbar^2k_\alpha}\delta(k-k_\alpha) \\ &= \frac{2\pi}{\hbar}\frac{L^3}{(2\pi)^3}\frac{mk_\alpha}{\hbar^2}d\Omega|V_{eff}(\mathbf{q}_\alpha)|^2. \end{aligned} \tag{4.76}$$

In the above

$$k_\alpha = \sqrt{k_i^2 - \frac{2m\Delta_\alpha}{\hbar^2}}, \tag{4.77}$$

[6] Again, $\mathbf{k}$ lies in a solid angle $d\Omega$ around certain direction $\hat{n}$.

and

$$\mathbf{q}_\alpha = k_\alpha \hat{n} - \mathbf{k}_i. \tag{4.78}$$

The differential cross section is given by

$$\frac{d\sigma}{d\Omega} = \frac{dW}{\frac{1}{L^3}\frac{\hbar k_i}{m} d\Omega} = \Big(\frac{m}{2\pi\hbar^2}\Big)^2 \frac{k_\alpha}{k_i} |V_{eff}(\mathbf{q}_\alpha)|^2 \tag{4.79}$$

Similar to the elastic scattering case, we can easily prove that

$$V_{eff}(\mathbf{q}_\alpha) = U(\mathbf{q}_\alpha) S_*(\mathbf{q}_\alpha), \tag{4.80}$$

where

$$S_*(\mathbf{q}_\alpha) = \int d^3r_1 ... d^3r_N \Phi^*_\alpha(\mathbf{r}_1, ..., \mathbf{r}_N) \Big(\sum_j e^{-i\mathbf{q}_\alpha \cdot \mathbf{r}_j} \Big) \phi_0(\mathbf{r}_1, ..., \mathbf{r}_N). \tag{4.81}$$

Put everything together we have, for inelastic scattering,

$$\frac{d\sigma}{d\Omega} = \Big(\frac{k_\alpha}{k_i}\Big)\Big(\frac{m}{2\pi\hbar^2}\Big)^2 |U(\mathbf{q}_\alpha)|^2 |S_*(\mathbf{q}_\alpha)|^2. \tag{4.82}$$

4.5 The decay of an excited atom:spontaneous emission

Consider an hydrogen atom enclosed in a cubic box of linear dimension L. The quantum mechanical degrees of freedom in this box involves the electrons in the atom,[7] and the harmonic oscillators associated with the electromagnetic field in the box. The electromagnetic waves represent the oscillation of the electric and magnetic fields. Due to the boundary condition of the box, the allowed wave vectors of the EM wave are

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_3). \tag{4.83}$$

[7]We shall assume the nucleus of the atom is fixed at the center of the box.

Associated with each allowed wave vector the EM wave can have two mutually orthogonal ploarizations[8] which are orthogonal to $\mathbf{k}$

$$\epsilon_{\mathbf{k}} \cdot \mathbf{k} = 0. \tag{4.84}$$

In classical E&M each of the allowed component of the electromagnetic wave is an normal mode of the electromagnetic oscillation in the box. In quantum mechanics each of these normal mode is a quantum simple harmonic oscillator (with the magnetic/electric fields play the role of x/p respectively). The Hamiltonian that describes the quantum electromagnetic oscillation inside the box is given by

$$H_{EM} = \sum_{\mathbf{k}} \sum_{\alpha} \hbar\omega_{\mathbf{k}} \left(a^{\dagger}_{\mathbf{k}\alpha} a_{\mathbf{k}\alpha} + \frac{1}{2} \right). \tag{4.85}$$

Here $a^{\dagger}_{\mathbf{k}\alpha}$ creates a photon with wave vector $\mathbf{k}$ and polarization α, and

$$\omega_{\mathbf{k}} = c|\mathbf{k}|. \tag{4.86}$$

Now let us come to the quantum mechanical description of the atom. In earlier part of quantum mechanics we have learned how to write down the Hamiltonian and eigen energies and eigen functions for the H-atom. As we have learned, H-atom has infinite many eigenstates. In this part of the lecture we shall simplify it by keeping only two energy levels, the ground state $^2S_{1/2}$ and one of the first excited state[9] $^2P_{1/2}$. Under this simplifying assumption the atom is described by

$$H_a = E_1 |e\rangle\langle e| + E_0 |0\rangle\langle 0|. \tag{4.87}$$

Here $|0\rangle$ and $|e\rangle$ represent the ground and excited states and $E_{0,1}$ are their respective eigen energies.

[8]The polarization of the electromagnetic wave represent the direction of the oscillating electric field. The direction of the oscillating magnetic field is perpendicular to the electric field. The electric and magnetic field oscillate out of phase analogous to the out-of-phase oscillation of the position and momentum of a simple harmonic oscillator.

[9]The reason we throw other first excited state away is because there is a "selection rule" that forbid them to decay to the ground state by emitting photon.

Thus if we ignore the interaction between the electromagnetic oscillation and the electron in the atom we have the following total Hamiltonian

$$H_0 = H_{EM} + H_a = \sum_{\mathbf{k}} \sum_{\alpha} \hbar\omega_{\mathbf{k}} \left(a^{\dagger}_{\mathbf{k}\alpha} a_{\mathbf{k}\alpha} + \frac{1}{2} \right) + E_1 |e\rangle\langle e| + E_0 |0\rangle\langle 0|. \tag{4.88}$$

The eigenstates of Eq. (4.88) are the direct product of the eigenstates of H_a and H_{EM}:

$$|\sigma, \{n_{\mathbf{k}\alpha}\}\rangle = |\sigma\rangle \otimes |n_{\mathbf{k}\alpha}\rangle. \tag{4.89}$$

Here $|\sigma\rangle = |0\rangle$ or $|e\rangle$ and

$$a^{\dagger}_{\mathbf{k}\alpha} a_{\mathbf{k}\alpha} |\{n_{\mathbf{k}\alpha}\}\rangle = n_{\mathbf{k}\alpha} |n_{\mathbf{k}\alpha}\rangle. \tag{4.90}$$

The state $|\{n_{\mathbf{k}\alpha}\}\rangle$ should be interpreted as having $n_{\mathbf{k}\alpha}$ photons with wave vector $\mathbf{k}$ and polarization $\epsilon_{\mathbf{k}\alpha}$.

The interaction between the electromagnetic field and the atomic electrons is given by

$$V = -e\mathbf{r} \cdot \mathbf{E}. \tag{4.91}$$

Here $\mathbf{r}$ is the position operator of the electron and $\mathbf{E}$ is the electric field at the position of the atom. When represented in the basis $|0\rangle$ and $|e\rangle$ the operator $e\mathbf{r}$ becomes a two by two matrix with vector matrix elements:

$$e\mathbf{r} \rightarrow \begin{pmatrix} 0 & \mathbf{p} \\ \mathbf{p} & 0 \end{pmatrix}. \tag{4.92}$$

The reason that the direct matrix element is zero is as follow. Since the upon spatial inversion (i.e. $\mathbf{r} \rightarrow -\mathbf{r}$) the H-atom Hamiltonian is invariant, the eigenstates of H_a are simultaneous eigenstates of the spatial inversion operator P_I. Thus

$$\begin{aligned} P_I |0\rangle &= \lambda_0 |0\rangle \\ P_I |e\rangle &= \lambda_e |e\rangle. \end{aligned} \tag{4.93}$$

Since $P_I^2 =$ identity (hence $P_I = P_I^{-1}$),

$$\lambda_{0,e} = \pm 1. \tag{4.94}$$

Now let us consider the matrix element $\langle 0|e\mathbf{r}|0\rangle$. Clearly

$$\begin{aligned}\langle 0|e\mathbf{r}|0\rangle &= \langle 0|P_I P_I^{-1} e\mathbf{r} P_I^{-1} P_I|0\rangle \\ &= \lambda_0^2 \langle 0|P_I^{-1} e\mathbf{r} P_I^{-1}|0\rangle = \langle 0|P_I e\mathbf{r} P_I^{-1}|0\rangle = -\langle 0|e\mathbf{r}|0\rangle. \end{aligned} \tag{4.95}$$

Here we have used the fact that upon spatial inversion $e\mathbf{r} \to -e\mathbf{r}$. Eq. (4.95) implies $\langle 0|e\mathbf{r}|0\rangle = 0$. Similar proof goes for $\langle e|e\mathbf{r}|e\rangle = 0$. Eq. (4.92) implies that

$$V = -\mathbf{E}\cdot\mathbf{p}\left(|e\rangle\langle 0| + |0\rangle\langle e|\right). \tag{4.96}$$

It takes some learning in quantum electrodynamics to show that

$$\mathbf{E} = \frac{g}{\sqrt{L^3}} \sum_{\mathbf{k}\alpha} \sqrt{\omega_{\mathbf{k}}}\epsilon_{\mathbf{k}\alpha}(a_{\mathbf{k}\alpha} - a_{\mathbf{k}\alpha}^\dagger). \tag{4.97}$$

Here g is a constant.[10] Since it is beyond the scope of this course to derive that we simply take this as given.[11] Thus the complete Hamiltonian that describes the quantum electrodynamics of a two-level atom is given by

$$\begin{aligned} H_{QED} &= H_0 + V \\ &= \sum_{\mathbf{k}}\sum_{\alpha} \hbar\omega_{\mathbf{k}} \left(a_{\mathbf{k}\alpha}^\dagger a_{\mathbf{k}\alpha} + \frac{1}{2}\right) + E_1|e\rangle\langle e| + E_0|0\rangle\langle 0| \\ &\quad - \frac{g}{\sqrt{L^3}} \left[\sum_{\mathbf{k}\alpha} \sqrt{\omega_{\mathbf{k}}}(\epsilon_{\mathbf{k}\alpha}\cdot\mathbf{p})(a_{\mathbf{k}\alpha} - a_{\mathbf{k}\alpha}^\dagger)\right] \left(|e\rangle\langle 0| + |0\rangle\langle e|\right). \end{aligned} \tag{4.98}$$

What we shall do is to treat the last term of H_{QED} as a perturbation and calculate the transition rate for the atom to decay from $|e\rangle$ to $|0\rangle$ by emitting a photon. Fermi golden rule implies that

$$W = \frac{2\pi}{\hbar} \sum_{\{n_{\mathbf{k}\alpha}\}} |\langle 0, \{n_{\mathbf{k}\alpha}\}|V|e, \{0\}\rangle|^2 \delta(E_1 - \sum_{\mathbf{k}\alpha} n_{\mathbf{k}\alpha}\hbar\omega_{\mathbf{k}} - E_0). \tag{4.99}$$

[10] g can be shown to be $-i\sqrt{\hbar/2}$

[11] One interesting thing is to note that the relation between the electric field and $a_{\mathbf{k}\alpha}^\dagger$ and $a_{\mathbf{k}\alpha}$ is similar to that between the momentum operator p and $a^\dagger, a$ in simple harmonic oscillator.

Using the expression of V in Eq. (4.98) we obtain

$$\begin{aligned} W &= \frac{2\pi}{\hbar}\frac{|g|^2}{L^3}\sum_{\mathbf{k}\alpha}(\mathbf{p}\cdot\epsilon_{\mathbf{k}\alpha})^2\omega_{\mathbf{k}}|\langle 0,\{0,0,..,1,0,..,0\}|(a_{\mathbf{k}\alpha}-a^\dagger_{\mathbf{k}\alpha}) \\ &\times(|e\rangle\langle 0|+|0\rangle\langle e|)\,|e,\{0\}\rangle|^2\delta(\hbar\omega_{\mathbf{k}}-\Delta). \end{aligned} \tag{4.100}$$

In Eq. (4.100) $\{0,0,..,1,0,..,0\}$ denotes the EM state in which there is one photon present in mode $\mathbf{k},\alpha$. The reason that we only need to consider one-photon final state is because V contains at most one photon creation operator. This photon can have any momentum $\mathbf{k}$ and polarization as long as the energy conservation

$$\hbar\omega_{\mathbf{k}} = \Delta \equiv E_1 - E_0 \tag{4.101}$$

is satisfied. Simple computation gives

$$W = \frac{2\pi}{\hbar}\frac{|g|^2}{L^3}\sum_{\mathbf{k}\alpha}\omega_{\mathbf{k}}(\mathbf{p}\cdot\epsilon_{\mathbf{k}\alpha})^2\delta(\hbar\omega_{\mathbf{k}}-\Delta). \tag{4.102}$$

Let $\theta_{\mathbf{k}}$ be the angle between $\mathbf{p}$ and $\mathbf{k}$ it is straightforward to prove that

$$\sum_{\alpha=1}^{2}(\mathbf{p}\cdot\epsilon_{\mathbf{k}\alpha})^2 = |\mathbf{p}|^2\sin^2\theta_{\mathbf{k}}. \tag{4.103}$$

Use the above result in Eq. (4.102) we obtain

$$\begin{aligned} W &= \frac{2\pi}{\hbar}\frac{|g|^2}{L^3}\int\frac{d^3k}{(2\pi/L)^3}(ck)|\mathbf{p}|^2\sin^2\theta_{\mathbf{k}}\delta(\hbar ck-\Delta) \\ &= \frac{2\pi}{\hbar}\frac{c|g|^2|\mathbf{p}|^2}{8\pi^3}\int d\Omega_{\mathbf{k}}\sin^2\theta_{\mathbf{k}}\int_0^\infty dk k^3\delta(\hbar ck-\Delta). \end{aligned} \tag{4.104}$$

Since

$$\int d\Omega_{\mathbf{k}}\sin^2\theta_{\mathbf{k}} = \int_0^{2\pi}d\phi_{\mathbf{k}}\int_0^\pi d\theta_{\mathbf{k}}\sin\theta_{\mathbf{k}}\sin^2\theta_{\mathbf{k}} = \frac{8\pi}{3} \tag{4.105}$$

we have

$$W = \frac{2\pi}{\hbar}\frac{|g|^2|\mathbf{p}|^2}{3\pi^2c^3\hbar}\omega_\Delta^3. \tag{4.106}$$

Here

$$\omega_\Delta = \frac{\Delta}{\hbar} \tag{4.107}$$

is the frequency of the emitted photon.

After obtaining the transition rate we can now compute the life time of the excited state. Imagine you have an ensemble of identical atoms all in the excited state $|e\rangle$ at time zero. Let $N_e(t)$ be the number of atoms that remain in the excited state after time t. Clearly we should have

$$\frac{dN_e(t)}{dt} = -WN_e(t). \tag{4.108}$$

The solution to the above equation is

$$N_e(t) = N_e(0)e^{-Wt} \tag{4.109}$$

which means that the life time of the excited state is

$$\frac{1}{\tau} = W. \tag{4.110}$$

Combine this with Eq. (4.106) we conclude

$$\frac{1}{\tau} = \frac{2\pi}{\hbar}\frac{|g|^2|\mathbf{p}|^2}{3\pi^2c^3\hbar}\omega_\Delta^3. \tag{4.111}$$

Thus the higher is the energy of the excited state the shorter it lives. As we discussed earlier in class, spontaneous emission is a consequence of the atom being disturbed by the quantum zero-point fluctuation of the EM field.

4.6 Stimulated emission

Now assume that initially the EM field is not in its ground state $|\{0\}\rangle$, instead it is in state $\{n_{\mathbf{k}\alpha}\}$. In this case Eq. (4.100) is modified to

$$W = \frac{2\pi}{\hbar}\frac{|g|^2}{L^3}\sum_{\mathbf{k}\alpha}(\mathbf{p}\cdot\epsilon_{\mathbf{k}\alpha})^2|\langle\{...,n_{\mathbf{k}\alpha}+1,...\}|a^\dagger_{\mathbf{k}\alpha}|\{...,n_{\mathbf{k}\alpha},...\}\rangle|^2\delta(\hbar\omega_{\mathbf{k}}-\Delta). \tag{4.112}$$

Recall that in simple harmonic oscillator

$$a^\dagger|n\rangle = \sqrt{n+1}|n\rangle, \tag{4.113}$$

as the result Eq. (4.112) gives

$$W = \frac{2\pi}{\hbar}\frac{|g|^2}{L^3}\sum_{\mathbf{k}\alpha}\omega_{\mathbf{k}}(\mathbf{p}\cdot\epsilon_{\mathbf{k}\alpha})^2(n_{\mathbf{k}\alpha}+1)\delta(\hbar\omega_{\mathbf{k}}-\Delta). \tag{4.114}$$

Note that for $n_{\mathbf{k}\alpha} = 0$ we recover the formula for spontaneous emission. If $n_{\mathbf{k}} \neq 0$, the emission rate is enhanced. In particular, if initially the number $n_{\mathbf{k}\alpha}$ of a particular normal mode is larger than that of all other normal mode (of course $\hbar\omega_{\mathbf{k}}$ must match Δ), it is more likely for the atom to emit such photon than all others.[12] This is as if the presence of photons in a particular normal mode *encourages* the atom to emit into that normal mode. This phenomenon is called "stimulated emission".

Stimulated emission is the principle of LASING. LASER is the abbreviation for light amplification by stimulated emission of radiation. For a LASER to work, we have to first achieve *population inversion*, i.e., having majority of the atoms in the excited state. The first atom that spontaneously emit creates a photon in a particular $\mathbf{k}, \alpha$ state. This photon stimulate atoms that de-excite later to emit photon into this same normal mode.

4.7 Absorption

In the absorption process, the atom is initially in the ground state $|0\rangle$ and the EM field is initially in the $|\{n_{\mathbf{k}\alpha}\}\rangle$ state. In this case Eq. (4.112) is modified to

$$W = \frac{2\pi}{\hbar}\frac{|g|^2}{L^3}\sum_{\mathbf{k}\alpha}(\mathbf{p}\cdot\epsilon_{\mathbf{k}\alpha})^2|\langle e,\{...,n_{\mathbf{k}\alpha}-1,...\}|a_{\mathbf{k}\alpha}|0,\{...,n_{\mathbf{k}\alpha},...\}\rangle|^2\delta(\hbar\omega_{\mathbf{k}}-\Delta). \tag{4.115}$$

Using the fact that in simple harmonic oscillator

$$a|n\rangle = \sqrt{n}|n-1\rangle \tag{4.116}$$

[12] Of course this is assume the energy $\hbar\omega_{\mathbf{k}\alpha}$ of this photon matches Δ.